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Biofouling and Design of a Biomimetic Hull-Grooming Tool

By

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14. ABSTRACT

Biofouling, the accumulation of biological detritus on a hard substrate, has plagued the United States Navy. Fouling causes increased hydrodynamic drag, resulting in increased fuel consumption and decreased speed and range. The purpose of this investigation was to research the formation of fouling, mechanisms of prevention, and tools for its removal. The Navy currently uses a copper-based antifouling coating that releases copper into the water, killing the fouling organisms. There is new research in biomimetic polymers that deter fouling, but are non-toxic. These polymers are rigidly attached to the hull surface extending their lifetime. Removal mechanisms have included water jets and abrasive brushes, yet no tool has concentrated on grooming the hull to remove the initial layer of microfouling. Removing the initial layer will deter the development of macrofouling, such as barnacles, which are more difficult to remove. The mechanisms that marine animals use to de-foul themselves were also examined and several concepts for a biomimetic hull-grooming tool were developed. These tools include novel brush designs; in addition, ultraviolet light was explored as another tool to remove microfouling.

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Abstract

Biofouling, the accumulation of biological detritus on a hard substrate, has plagued the United States Navy. Fouling causes increased hydrodynamic drag, resulting in increased fuel consumption and decreased speed and range. The purpose of this investigation was to research the formation of fouling, mechanisms of prevention, and tools for its removal. The Navy currently uses a copper-based antifouling coating that releases copper into the water, killing the fouling organisms. There is new research in biomimetic polymers that deter fouling, but are non-toxic. These polymers are rigidly attached to the hull surface extending their lifetime. Removal mechanisms have included water jets and abrasive brushes, yet no tool has concentrated on grooming the hull to remove the initial layer of microfouling. Removing the initial layer will deter the development of macrofouling, such as barnacles, which are more difficult to remove. The mechanisms that marine animals use to de-foul themselves were also examined and several concepts for a biomimetic hull-grooming tool were developed. These tools include novel brush designs; in addition, ultraviolet light was explored as another tool to remove microfouling.

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This report is the culmination of work conducted by a student hired under the National Research Enterprise Intern Program sponsored by the Office of Naval Research. This program provides an opportunity for students to participate in research at a Department of Navy laboratory for 10 weeks during the summer. The goals of the program are to encourage participating students to pursue science and engineering careers, to further education via mentoring by laboratory personnel and their participation in research, and to make them aware of Navy research and technology efforts, which can lead to future employment.

At the Naval Surface Warfare Center Carderock Division, the single largest employer of summer interns is the Center for Innovation in Ship Design (CISD), which is part of the Ship Systems Integration and Design Department. The intern program is just one way in which CISD fulfils its role of conducting student outreach and developing ship designers.

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Executive Summary

Biofouling refers to the adherence of marine organisms and biological detritus on hard surfaces in the marine environment. Its presence on ship hulls has plagued these sea-going vessels since their conception. Fouling causes increased hydrodynamic drag contributing to a reduction in speed and range, leading to a huge expenditure of fuel costs. It is estimated that vessel speed is reduced by up to 10 percent leading to a 40 percent increase in fuel consumption.[1] It is estimated that fouling costs the United States Navy one billion dollars per year.[2] Currently, there is a need to develop coatings that can effectively prevent fouling and to develop autonomous vehicles that can quickly and efficiently clean ship hulls. Recent regulations have barred the use of organotin compounds such as tributyltin (TBT) and copper-based paints, which are currently used by the Navy and have become the focus of increasing environmental regulation due to their slightly toxic nature. Organotin compounds are poisonous to the environment and to humans. Copper is particularly effective at limiting adhesion of fouling organisms due to its biostatic properties, but its use will likely be limited forcing researchers to develop eco-friendly antifouling coatings.

Recent research in antifouling polymers has attempted to exploit the properties used by the fouling organisms to adhere to the surface to develop a strong polymer that will not peel off of the ship hull in the marine environment while repelling fouling. Fouling release polymers such as silicones have also been explored as viable alternatives to copper-based coatings.

Even the best antifouling coating will eventually accumulate some biological material over time and so it is also necessary to develop underwater hull cleaning tools. Currently, the Navy uses brushes to scrape detritus from the hulls, which requires divers to operate the equipment. New autonomous underwater vehicles for hull cleaning have been developed, but their effectiveness has yet to be tested. Furthermore, the possibility of creating a biomimetic device, one that mimics the mechanisms used by marine organisms to de-foul themselves, has yet to be explored.

Several concepts for a biomimetic hull-grooming tool and the use of ultraviolet light to kill fouling have been proposed. These designs were analyzed based on coating protection, ease of use, and time of application. The design recommendations are submitted as part of this report for further consideration.

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[1] MarEx newsletter. *A New Way to Battle Barnacles.* http://www.newsletterscience.com/marex/readmore.cgi?issue_id=251&article_id=2356&1=1&s=54060.
[2] Callow, Maureen E and James A Callow. "Marine Biofouling: A Sticky Problem." *Biologist.* Vol. 49 No. 1. University of Birmingham. United Kingdom, 2002. p. 1.

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Introduction

Objectives

The first objective of this project was to conduct a literature review of the development of biofouling on Navy ships, current methods of prevention and control, and antifouling mechanisms used by marine organisms. The literature review involved analyzing scientific papers to determine how biofouling develops and evaluating mechanisms marine organisms use to attach to a hard substrate such as a ship's hull. This study also included a review of new developments in the coating protection in light of the increased scrutiny on copper-based paints due to their slight toxicity. Cleaning mechanisms were also reviewed including an analysis of the SCAMP brush system that the Navy primarily uses to clean ships' hulls. Finally, mechanisms used by marine organisms to rid themselves of fouling were reviewed in order to develop a biomimetic tool concept the Navy can use to clean the hull surface.

The second objective was to develop several conceptual designs for a biomimetic hull-grooming tool. Using the information collected on antifouling behavior of underwater mammals, several preliminary conceptual designs for a hull-grooming tool were developed. Multiple ideas for cleaning tools were developed and their viability was assessed based environmental impact, coating protection, time of application, and ease of use. Several brush designs were developed and their risk factors were assessed. These risk factors were similar to the design criteria and included environmental effects, effect on operational and war fighting capabilities, and time of application. An optimal brush design removes the fouling efficiently with minimal damage to the coating. The unloading of coating into the water has been under increased environmental regulation due to the toxicity of copper-based paints, the primary coating used by the Navy. These design recommendations are submitted as part of this report for further review and concept development.

Development of Fouling

Biological Composition and Development of Fouling

Biofouling consists of two main components—microfouling and macrofouling. Microfouling refers to the formation of a biofilm and adhesion surface, and macrofouling refers to the attachment of organisms such as barnacles, mussels, diatoms, and seaweed to produce a fouling community. The stages of fouling can be divided into four parts—biochemical conditioning, bacterial colonization, colonization by unicellular eukaryonts, and colonization by multicellular eukaryonts. Biochemical conditioning refers to the adsorption of chemicals followed by the absorption of macromolecules on the surface of the fouled object. Bacteria propel themselves to the hull using their flagella. They first encounter a layer of water molecules and penetrate this film using microturbulence achieved by the beating of the flagella. While the bacterial cell surface and the macromolecular film are both negatively charged, these electrostatic repulsions can be overcome through the secretion of polysaccharide fibrils that bring the bacterial cells to the surface. Bacteria attach to the surface by forming covalent bonds between the bacteria glycoxalic and macromolecular phase. The growing bacteria and the chemicals they secrete make up the microfouling, also referred to as "slime," which develops within a few hours of an object's immersion in water. The term "grooming" describes the removal of this initial layer of microfouling, or slime, from the surface.[3]

Within a few days, macrofouling develops as unicellular eukaryonts colonize the surface. These organisms include yeast, protozoa, and diatoms. Multicellular eukaryonts begin colonizing the surface within several weeks and include the settlement of meroplankton larvae and algal spores. One hypothesis is that the fouling in one stage promotes the fouling in the next stage. For instance, the creation of a biofilm composed of high energy compounds like proteins and sugars may attract bacteria promoting their colonization. Cleaning refers to the removal of macrofouling and requires significantly higher cost expenditures than grooming due to the strong adhesion of unicellular and multicellular eukaryonts.

The mechanism of adhesion involves two parts—the wetting of the substrate by the adhesive and the curing of the adhesive.[4] The wetting process determines the actual area of contact between the organism and the surface. The curing process sets up the microstructure of the film, which determines its adhesive properties and chemical strength. For example, in the alga *Enteromorpha*, one of the major fouling organisms, attaches to new surfaces by secreting an adhesive. It is attracted to the surface by its wettability and topography as well as a stimulus such as light.[5] Thus, this substantiates the claim that a rough surface increases the number of microniches for an organism to settle resulting in the accumulation of increased fouling. The adhesion strength of

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[3] Wahl, Martin. "Fouling and antifouling: some basic aspects." *Marine Ecology Progress Series*. Vol. 58. 175-189. Zoologisches Institut, Universitat Kiel. Federal Republic of Germany, 1989.
[4] Callow, p.2
[5] Ibid., p. 2.

Enteromorpha is 500 mN $m^{-2.}$ Once the organism wets the surface with adhesive, it is cured by cross-linking thereby increasing its tensile strength. Cross-linking refers to the close packing of the polymer chains, which is characterized by its strong chemical bonds that are unlikely to degrade. This process of wetting and curing of the adhesive has been dubbed "first kiss."[6] Barnacles follow a similar process of "first kiss." They begin as cyprids and require a hard surface for development into adult barnacles. Cyprids use their antennules to examine a surface; once they have settled on a surface, the antennules secrete an adhesive onto the substrate. This adhesive also acts a signal to stimulate the arrival of more cyprids to the surface. The curing process involves the release of proteinaceous cement onto the antennules eventually calcifying the organism into a hard barnacle.

Biochemical Basis of Fouling

The transmission of chemical signals between larvae causes the accumulation of macrofouling, which is primarily responsible for the large costs of biofouling.[7] Two classes of chemical signaling molecules have been observed—mimics of the GABA neurotransmitter (γ aminobutyric acid) and an amino acid moiety, a part of a larger biomolecule, which contains DOPA. The GABA-mimetic molecule is secreted by cynobacteria and red algae. There are two distinct pathways that control the settlement and metamorphosis of the *Haliotis* genus of larvae. The Trigger or Morphogenetic pathway involves the binding of GABA to a GABA chemosensory receptor on the cell surface. This activates cyclic AMP, which opens calcium and other ion channels leading to the depolarization of the cell and the transduction of the signal. This pathway is responsible for the metamorphosis of the plankton larvae. The Regulatory or Amplifier pathway amplifies the result of the morphogenetic pathway. It is a second-messenger pathway that involves the binding of a specific group of amino acids to their receptor, the activation of a G-protein (guanine protein), followed by the activation of diacylglycerol (DAG), and a protein kinase. The interaction between the two pathways increases the sensitivity of the larvae and prepares them for settlement and metamorphosis.

One of the most notorious fouling organisms is polychaetes, which release a strong, adhesive cement onto the surface. For example, *Phragmatopoma californica* forms fouling communities containing thousands of organisms in cemented sand. The settlement of additional larvae is facilitated by chemosensory recognition of the inducer associated with the cement. This cement is composed of a DOPA-rich quinone, similar to the DOPA protein contained in the adhesive byssus threads of the marine mussel. Mussels use the adhesives in these byssus threads to attach to a hard substrate.

Once the biochemical pathways have been characterized, it is possible to determine what chemicals will inhibit them and prevent the development of large fouling communities. For example, halogenated hydrocarbons similar to the fluoropolymers that have been used today were successful in preventing the attachment and metamorphosis of *H.*

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[6] Callow, p.4.
[7] Morse, Daniel E. "Biochemical control of marine fouling." Defense Technical Information Center. University of California at Santa Barbara. March 1980-January 1988.

rufescens larvae at low concentrations. In addition, molecules with slight stereochemical dissimilarities to GABA can block the settlement of *H. rufescens* larvae. However, the effectiveness of these molecules has not been tested in subsequent studies. Lectins, or sugars, specific to mannosyl and glycosyl derivatives were founded to completely inhibit the settlement of these larvae. Yet questions about how effective these inhibitors are against other organisms with potentially different signaling pathways remains to be seen. Thus, the best mode of attack against fouling is not a specific chemical that blocks one signaling pathway, as there is a vast multitude of fouling organisms with many different signaling pathways.

Antifouling Coatings

Types of Coatings

Three different types of coatings have been developed to deter the accumulation of fouling including antifouling, fouling release, and epoxy coatings. Antifouling (AF) coatings contain biocides that are meant to erode, or ablate, over time. The erosion of the coating allows for the release of the biocide to directly kill the fouling organism. Copper is an antifouling coating currently used on Navy ships. A grooming tool targeted for an AF coating would have to be minimally aggressive to prevent the ablation of copper paint. Not only is the toxicity of the paint a cause for concern, but the increased ablation of the paint by an overly aggressive grooming tool would limit the effective life of the coating.

Fouling release coatings are hydrophobic, low surface energy, nontoxic coatings. Surface energy refers to the interruption of chemical bonds on a surface. The degree of wetting depends on the relationship between the forces of cohesion and adhesion where wetting refers to the spread of a liquid over a surface. Hydrophobic coatings are often used in fouling release coatings because they result in a larger contact angle between the organism's glue and the surface; a larger contact angle results in less wettability and less fouling because the glue cannot spread across the surface. Their highly flexible backbone allows them to maintain a low surface energy arrangement. Figure 1 shows the structure of polydimethylsiloxane (PDMS), a silicone-based polymer. The compound is low-energy and highly stable due to the strength of the silicon-oxygen bond. Further, the strength of the silicon-oxygen bond makes the compound fairly unreactive and a good fouling release polymer.

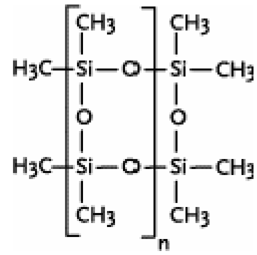

Figure 1: A silicone fouling release polymer illustrating the flexible backbone consisting of silicone-oxygen bonds.

Their smoothness reduces the presence of microniches where organism can settle, a factor known as the thigmotactic nature of settlement. Fouling release coatings such as Intersleek and silicone coatings lower the adhesion strength of glues secreted by fouling organisms. As soon as the ship begins moving the water, the hydrodynamic force causes the organisms to wash away. However, fouling release coatings are not efficient on Navy ships that remain at port for months at a time; by this point, the growth becomes so thick that the organisms do not wash away easily. The Intersleek 900 is a new fouling release coating with a fluoropolymer chemical makeup. Its amphiphilic nature means that the chemical and electrostatic adhesion between the surface and the fouling organism is minimized. Furthermore, it allows for a large enough contact angle such that complete wetting will not occur and fouling will be minimized. Figure 2 shows how the degree of wetting is minimized with Intersleek 900.

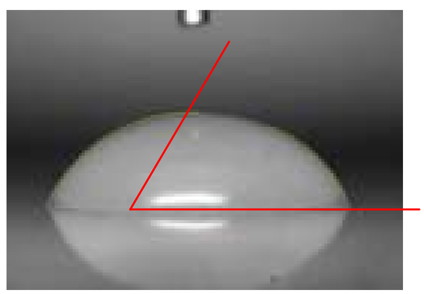

Figure 2: The formation of a liquid droplet on the Intersleek 900 with contact angle indicated.

The third type of antifouling coating is a two-part epoxy coating that is highly durable, but does not prevent marine growth. It is advantageous in that a highly aggressive cleaning action can be applied without damage to the coating. However, the hulls must be groomed regularly since the development of even a small amount of growth would be extremely difficult to remove. This is because the coating does not possess any antifouling properties and thus it is difficult to remove any fouling as there is nothing to deter the adhesion of fouling organisms.

Biomimetic Antifouling Polymer Materials

Biomimetic polymers have been the subject of research on antifouling coatings. The University of Birmingham in the United Kingdom and Northwestern University have researched biomimetic polymers modeled on the adhesives secreted by mussels to adhere to hard surfaces.[8] The adhesion mechanism of mussels, specifically *Mytilus edilus,* involves the release of byssal threads composed of collagen and silk-like proteins. The byssus is first secreted as a proteinaceous liquid that subsequently hardens rapidly.[9] The 3,4-dihydroxyphenylalanine (DOPA) amino acid polymer was found to be the amino acid primarily responsible for adhesion, as it is not found in many compounds outside of mussel adhesive proteins (MAPs.) The unoxidized form of DOPA initially adheres to the surface and further oxidation to DOPA-quinone yields a cross-linked network for increased strength. In some experiments, the strength of synthetic polymers was greater than the strength of the proteins secreted by mussels themselves.[10]

This research group used an mPEG-DOPA$_x$ polymer consisting of a linear set of PEG (polyethylene glycol) monomers where x = 1-3 DOPA residues conjugated to the ends (See Figure 4). The DOPA end serves as an adhesive moiety, which functions as a surface anchor for attaching the polymer to the hull. The polyethylene glycol (mPEG) portion functions as an antifouling polymer. The result is an extremely durable polymer that will remain intact on the ship for an extended period of time. The ability of the polymer to resist fouling was tested by placing it in cell culture with fibroblasts for four hours. This polymer was attached to a titanium surface, which is commonly used for its anti-corrosion and high strength properties. The mPEG-DOPA$_1$ polymer showed a decrease in cell attachment showing its potential as an antifouling polymer. Increasing the number from DOPA residues from one to three also increases its effectiveness as an anti-fouling polymer by increasing its adhesive strength.

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[8] Callow, p.1
[9] Dalsin, Jeffrey L. and Philip B. Messersmith. "Bioinspired antifouling polymers." *Materials Today*. p. 38-46. September 2005. p. 39.
[10] Ibid., 40.

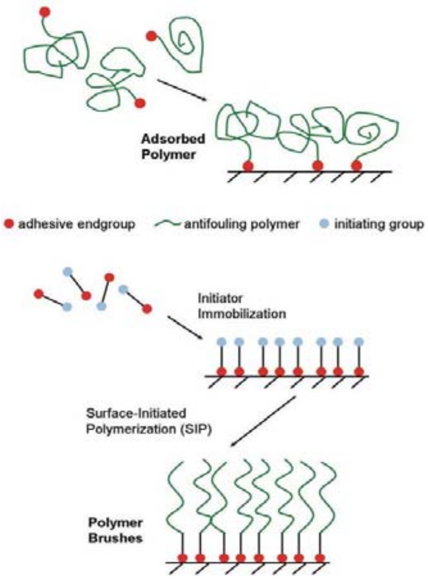

Figure 3: Mechanism of attachment of mPEG-DOPA antifouling polymer. The DOPA-containing compound is the adhesive endgroup and the antifouling polymer is mPEG.

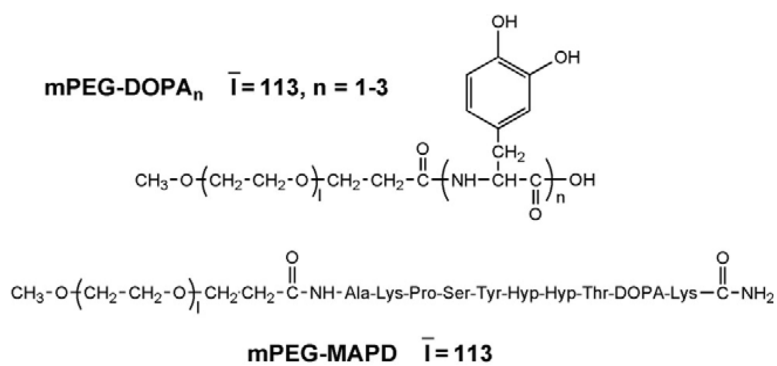

Figure 4: Structure of DOPA-containing polypeptide.

While mPEG-DOPA showed resistance to the cell attachments for several hours, it is susceptible to oxidative cleavage over time and so peptidomimetic polymers have also been examined.[11] (Oxidative cleavage would result in the degradation of the polymer and loss of antifouling ability.) PMP1, for example, consists of an *N*-substituted glycine residue attached to a short peptide that adheres to the surface. These polymers were also placed in fibroblast culture but with a duration of five months. In general, good antifouling polymers contained hydrogen bond acceptors, lacked hydrogen bond donors, were neutrally charged, and were soluble in water.

The properties of mPEG-DOPA were further examined by determining its resistance to

[11] Ibid., 43.

algal fouling. The polymer was plated onto a titanium-coated silicon wafer substrata and the level of cell attachment to the green alga *Ulva linza* and *Navicula perminuta* were examined. There was a significant decrease in the amount of cell attachment on these plates as compared to the two control groups. One apparent shortcoming in this analysis was that the properties of PEG as an antifouling polymer have not been thoroughly studied. Nevertheless, the mPEG-DOPA polymer showed considerably less cell attachment than the silicone polymer, which has been another subject of research in anti-fouling coatings.

Another biomimetic polymer is zosteric acid, a derivative of eel grass, that interferes with the mechanism of adhesion to inhibit the accumulation of fouling. It is possible to synthesize non-stick polymers having the same properties as organisms that remain free of fouling. The Office of Naval Research sponsored Karen Wooley, a polymer chemist at Washington University in St. Louis who synthesized a polymer consisting of PEG and another branched, fluorinated, hydrophobic polymer that simulates the mountain and valley terrain of a dolphin's skin.[12] Wooley also examined a Teflon coating; however, Teflon was not considered as an antifouling polymer because barnacles easily attach to Teflon fibers.

Researchers in Germany created a covalently cross-linked gel modeled on the skin of a pilot whale.[13] The dolphin's physical defenses include desquamation or peeling off of different parts of the body's surface, ritual cleaning, and the secretion of mucus. Dolphin skin also contains low surface tension and its smooth skin reduces the number of microniches in which fouling organisms can embed themselves. The remaining hurdles lie in producing these polymers on a mass scale and testing their efficacy outside of the microscale dimensions used in the lab.

In 2005, the Naval Research Laboratory conducted testing of fouling-release coatings for warships.[14] Coatings can be evaluated in terms of the following properties—surface energy, mechanism by which the coating attaches, and the thickness of the coating. Fluorinated fouling release coatings contain closely packed fluorinated groups that decrease its surface energy and repel the formation of fouling. Their eventual failure arises from shear stress at the interface between the foulant and coating. Silicone polymers, however, were found to work better than fluorinated polymers. They are characterized by low surface energy and possess the lowest elastic modulus (mechanism of attachment to the surface). Silicone polymers are smooth, are resistant to hydrolysis, and remain stable underwater. A smooth surface is critical in any antifouling polymer as a polymer with rough edges will facilitate the embedding of fouling organisms. It should be noted that the mPEG-DOPA polymers showed greater resistance to algal fouling than

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[12] http://www.scienceblog.com/cms/node/818/print
[13] Baum, C. et al. "A covalently cross-linked gel derived from the epidermis of the pilot whale *Globicephala melas*." *Biorheology*. (39) p. 703-717. 2002.
[14] Brady, Robert F. "Fouling-release coatings for warships." Naval Research Laboratory, Washington D.C. *Defence Science Journal.* Vol. 55 No.1 pp.75-81. 2005.

the silicone polymers.[15]

Most recently, carbon nanotubes have been identified as a possible antifouling coating. The new coating was presented at the EuroNanoForum in Dusseldorf, Germany. Carbon nanotubes are mixed with silicone paint, which serves to denature the adhesive glue secreted by fouling organisms. As a result, the fouling falls away once the vessel is in motion.[16] However, the use of this technology poses a problem for Navy ships that remain stationary for extended periods of time.

Biological Cleaning Mechanisms of Marine Organisms

General Defense Mechanisms

Marine organisms have also developed mechanisms to remove fouling from their appendages. Mechanical defenses include special surface structures such as spicules (a sharp, pointed body part) and the production of mucus that wipes away the fouling organisms. The organism spreads the mucus across its body in a windshield wiper-like effect. Scraping of the surface containing fouling organisms with special appendages by the picking activity of echinoderm pedicellaria, byrozoan avicularia, and vibracularia is also a prevalent defense mechanism.[17] Chemical defenses include extreme pH values and the secretion of metabolites such as toxins to kill fouling organisms. Physical defenses include a methylated or fluorated epidermis, which acts like an antifouling polymer. The high degree of cross-linking is characterized by tightly packed bonds; subsequently, the chemicals secreted in the adhesives of fouling organisms cannot penetrate the close packing and eventually fall off as the organism moves through the water.

Grooming Techniques of Crayfish, Crab, and Shrimp

Marine organisms, particularly crustaceans, use a variety of grooming techniques to remove fouling. For example, crayfish, specifically *Procambarus clarkii*, engage in limb rocking to clean their gills. Limb rocking occurs when a crayfish lifts four of its pereopods in different combinations and sways back and forth while its body remains in place. The setobranches then jiggle among the gill filaments. The podobranches cause the setobranch setae at the posterior and medial sides of the podobranches to be pushed and pulled as well.[18] The movement of setobranch setae is aided by podobranch gills on limb coxae that push and pull the setae. The setobranch setae are also digitated with smaller setules or tufts of bristles that further aid in grooming (See Figure 5). However, this mechanism does not entirely remove the fouling from the crayfish as only molting

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[15] Statz, Andrea et. al. "Algal antifouling and fouling-release properties of metal surfaces coated with a polymer inspired by marine mussels." *Biofouling.* 22(6). p. 391-399.
[16] MarEx newsletter. *A New Way to Battle Barnacles.* http://www.newsletterscience.com/marex/readmore.cgi?issue_id=251&article_id=2356&1=1&s=54060.
[17] Wahl, 183.
[18] Bauer, Raymond T. "Gill cleaning mechanisms of the crayfish *Procambarus clarkia* (Astacidea: Cambaridae): experimental testing of setobranch function." *Invertebrate Biology.* 117(2): 129-143.

completely eradicates the fouling. Crayfish also engage in generic brushing using their setobranches, which are digitated with small setules. Setules are smaller brushes that also aid in grooming. Cheliped brushing, which involves the use of claws to scrape the fouling, is also a common feature of the antifouling defenses of the crayfish.

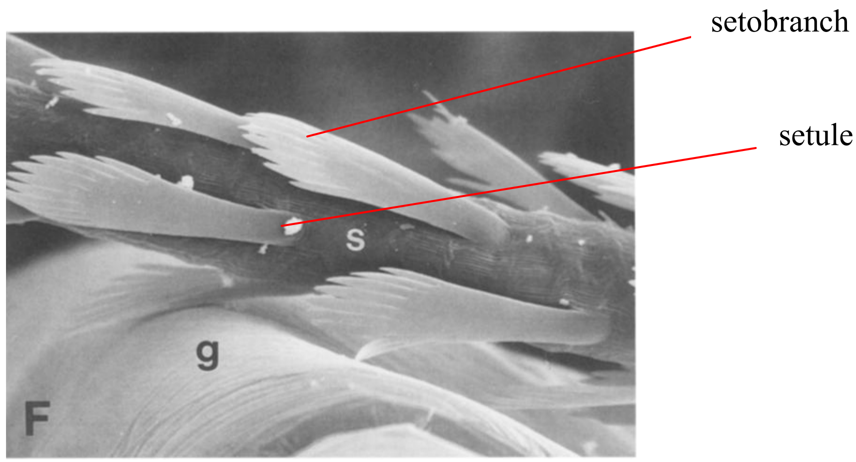

Figure 5: Setobranch seta of *Procambarus clarkii* with digitate scale setules.

Grooming mechanisms of the dendrobrachiate shrimp, *Rimapenaeus similis,* primarily include structures containing multidenticulate setae. They also possess unique digitate scale setules that resemble hands with elongated fingers. The use of multidenticulate setae allows for a more efficient grooming action.

Figure 6 shows the digitate scale setules on the shaft of epipodal setae. In some pereopods, the exopods were modified into a flattened form that sweeps back and forth over the gills. Chelipeds with brushes of setae attached are a more vigorous cleaning mechanism. Like the crayfish, however, molting was the only complete escape from epibiotic fouling.

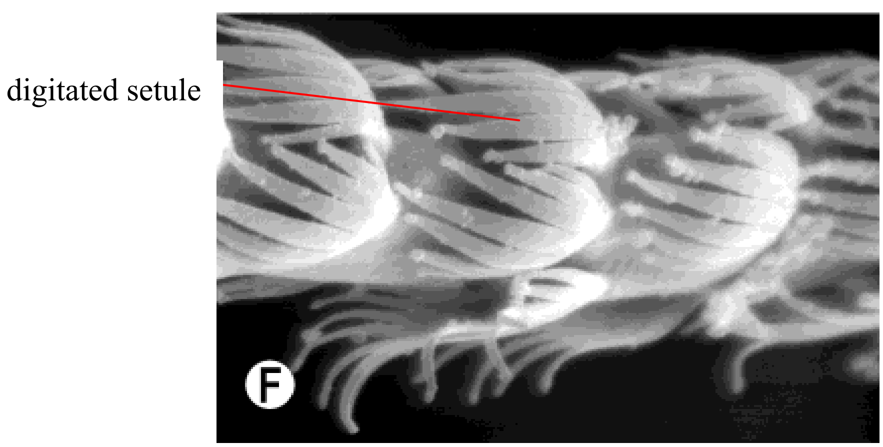

Figure 6: Digitate scale setules on shaft of epipodal setae.

The amphibious freshwater crab, *Geothelphusa dehaani*, engages in similar gill cleaning

behavior but uses markedly different structural appendages. The crab engages in limb rocking in which it agitates its limbs while the rest of its body remains stationary. Cheliped brushing involves directly picking out the fouling using its claws. Two types of setobranch setae are common in the crab—anchor and brush setae. Anchor setae are anchor-like outgrowths from the epipods while brush setae assist in scraping fouling attached to the anchor setae. Their opposing recurved ends are able to cover a large surface area and allow for bidirectional scraping, making it an efficient scraping design. A unique feature of the epipod brushing system is their agitation as a result of a maxiliped lever system. The movement of the endopod causes the displacement of the epipod resulting in the coverage of a larger surface area and more forceful agitation.

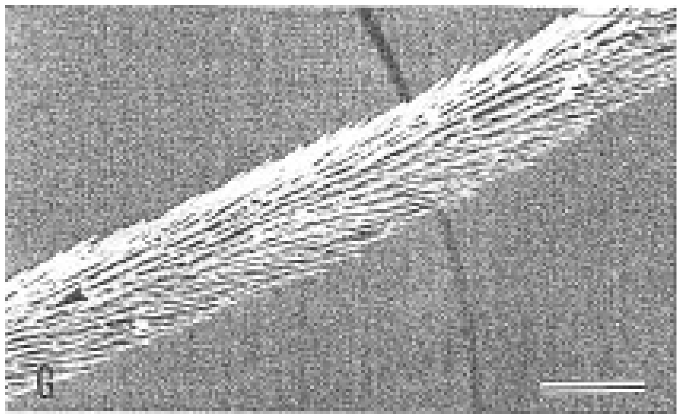

Figure 7: Brush seta surrounded by spine-like setules.

Mechanical Equipment for Underwater Hull Cleaning

Navy Hull Cleaning Methods

Currently, the Navy uses the SCAMP brush system to clean hulls. However, this system releases paint into the water, which poses an environmental hazard.[19] SCAMP consists of three rotary brushes positioned in a triangular array. The advantages of the SCAMP system include the high speed of rotation of its three brushes and the fact that it adheres to the hull by creating a vacuum whereby the water is suctioned through an impeller and expelled. Additionally, single brush and multi brush units are available. These brushes are typically made of synthetic materials such as nylon and polypropylene. Other cleaning tools authorized by the Navy include abrasive hand pads and water jets. Hand tools are used to remove fouling from hard-to-reach areas.[20] Depending on the ship component, a different tool is authorized for cleaning that part of the ship. For instance, wooden hand scrapers are authorized for the cleaning of any part of the ship's hull with the exception of the bilge keels. Only specific models of multi-brush units are authorized

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[19] Kalmuck, K.M. et al. "Development of a DynaJet Cavitating Water Jet Cleaning Tool for Underwater Marine Fouling Removal." 9th American Waterjet Conference. August 23-265, 1997. Dearborn Michigan. p. 541-554.

[20] Naval Ships Technical Manual 081. *Waterborne Underwater Hull Cleaning of Navy Ships.* S9086-CQ-STM-010. Rev. 5. 01 Oct 2006.

to clean a majority of hull components and are permitted only when the hull curvature allows for a multi-brush system. Multi-brush units are not permitted in cleaning of propellers although single brush units (polyester or polypropylene) may be used in addition to Scotch Brite™ pads and scrapers. Due to the configuration of Navy ships, all cleaning tools must be diver-operated.[21]

Navy guidelines mandate that the least aggressive brush for hull cleaning be used while preventing any damage to the coating. Cleaning of the hull should not result in the presence of scratch or swirl marks. The quality of hull cleaning is evaluated based on photographs taken before and after the cleaning. Underwater television systems may also be used to allow for communication between the decision maker on deck and the diver to evaluate the quality of cleaning.

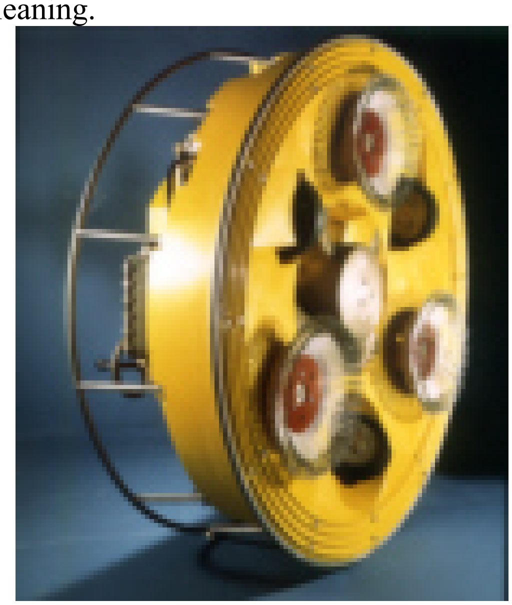

Figure 8: SCAMP hull cleaning tool.

DynaJet Cavitating Water Jet[22]

A cavitating water jet induces a vapor filled cavity in a liquid jet that collapses into a high-pressure jet. The energy from the collapse of each bubble is concentrated over a tiny area allowing for a localized stress that aids in the removal of fouling. Softer surfaces result in the less violent collapse of cavities and so the softer paint on the hard surface is not damaged. The apparatus was tested on three different panels, one with a fouling stimulant, the second with copper-based antifouling paint, and a third panel fouled with marine growth. To achieve the requisite cleaning surface area, a Mosmatic Turbo-Rotor Heavy Duty Swivel and T-Bar were used. This apparatus consists of a rotating swivel join with two arms extending radially outwards at a 90 degree angle. The

[21] Ibid., 81-4-1.
[22] Kalmuck, K.M. et al. "Development of a DynaJet Cavitating Water Jet Cleaning Tool for Underwater Marine Fouling Removal." 9th American Waterjet Conference. August 23-265, 1997. Dearborn Michigan. p. 541-554.

results showed that fouling was removed at pressures as low as 3.5 MPa. Very little damage to the paint was caused, even at a pressure of 21 MPa, and so the use of this equipment would eliminate the need for a large scale filtering system to remove potentially toxic contaminants from the paint coating the ships.

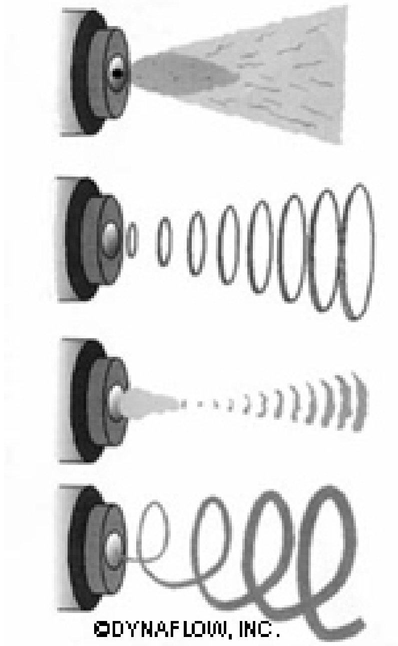

Figure 9: Various models of water jets developed by DynaJet for fouling removal

General Cleaning Tools

Other devices include the AURORA underwater climbing robot, which includes a manned control center and has demonstrated effectiveness in testing. An underwater robot, underwater cleaning apparatus with suction cup, and high-pressure water have been awarded patents; however, the viability of these cleaning tools has not been confirmed. Another method kills barnacle larvae in water by irradiating them with UV light. However, the ecological impacts of this technique have not been examined.

A vibrotechnological device consists of an unmanned robot that moves using a rubber caterpillar drive to move along the hull and contains a vibrating bulldozer blade for the removal of fouling. The advantage of the bulldozer blade is that it adjusts to accommodate the level of fouling on the hull. The levels are divided into three parts—the primary layer consists of low-density plants and mud, the secondary layer is composed of algae, and the tertiary layer consists of mollusks. Furthermore, the tool is attracted to the hull by magnetic forces allowing for stability. Bulldozer cleaning can be performed faster than a rotary brush while using less energy. The disadvantages include decreased quality of cleaning with only one travel of the blade as opposed to a rotary

brush.[23]

Biomimetic Hull-Grooming Tool Development

Design Considerations and Evaluation

The second phase of this project involved using the literature research concerning the grooming and cleaning mechanisms of animals to develop concepts for a biomimetic hull-grooming tools. The advantage of a grooming tool is that it uses a non-aggressive means of removing the initial layer of fouling to prevent the growth of hard fouling that is much more difficult to remove. Grooming tools have not been thoroughly studied as most efforts in antifouling have concentrated on cleaning tools. As noted in the discussion of the biochemical basis of fouling, the adhesive cement serves as a signal to attract other fouling organisms to the site. Thus, the removal of this initial slime will inhibit the development of fouling communities. The grooming tools will be mounted on an autonomous underwater vehicle that traverses the hull.

The initial phase of concept development involved brainstorming several different ideas for the removal of fouling and then evaluating those ideas based on specified requirements. The criteria included environmental friendliness, coating protection, ease of use, compatibility with today's standards, and visual inspection capability. Environmental friendliness refers to the impact of the grooming tool on the marine ecosystem. Ease of use refers to the simplicity of the mechanism for the operators. Coating protection refers to the aggressiveness of the grooming tool and whether this aggressiveness will result in significant ablation of the coating. The Navy currently uses antifouling coatings that are meant to ablate over time to allow release of the biocide; however, a highly aggressive cleaning tool will result in an increase rate of ablation thereby lowering the effective life of the coating. The autonomous vehicle on which the grooming tool will be mounted requires a simplistic, low power, low energy tool that is cost-effective. Compatibility with today's standards refers to whether the technology behind the grooming tool exists and if not, the ease with which it could be developed. Visual inspection capability refers to the ability to immediately determine whether the grooming tool has removed the slime. For instance, certain mechanisms might weaken the adhesion between the slime and hull but the slime only falls away when the ship is in motion. Consequently, immediate visual inspection of the hull is impossible. The importance of each of these factors was determined by evaluating them against each other using a pairwise comparison chart.

[23] Sulcs, A. and O. Verners. "Vibrotechnological underwater cleaning of ship hulls." 4th International DAAAM Conference. 29-30th April 2004. Tallinn, Estonia.

Table 1: Pairwise Comparison Chart.

Pairwise comparison	**Environmentally friendly**	**Coating protection**	**Ease of use**	**Time of application**	**Compatibility with today's standards**	**Visual inspection capability**	Total	%
Environmentally friendly		4	5	5	5	5	24	26.67
Coating protection	2		4	4	5	4	19	21.11
Ease of use	1	2		2	4	3	12	13.33
Time of application	1	2	4		3	3	13	14.44
Compatibility with today's standards	1	1	2	3		4	11	12.22
Visual inspection capability	1	2	3	3	2		11	12.22
						Total	90	100

The criteria in the rows were ranked against each of the criteria in the columns on a scale of 1-5 with 5 indicating that the criterion in the row was significantly more important the than the criterion in the column. For example, environmentally friendly versus ease of use was a 5 because environmental friendliness was judged to be significantly more important than ease of use. Environmental friendliness and coating protection had the largest scaled score and so these were the two most important criteria in determining the validity of a product idea.

After determining the importance of the criteria, the product designs were evaluated based on criteria on a scale of 0-5, with a score of 5 indicating that the design maximally fulfilled the criterion (Table 2.) A score of 0 was given to those ideas whose merits could not be conclusively evaluated. While a final evaluation of these criteria cannot be done until the products are actually tested, this preliminary evaluation was useful in determining the potential merits of the designs.

Table 2: Weighted Decision Matrix.

The percentages at the top refer to the weighting of each decision factor.

	26.67%	21.11%	13.33%	14.44%	12.22%	12.22%	
Weighted Decision Matrix	**Environmentally friendly**	**Coating Protection**	**Ease of use**	**Time of application**	**Compatibility with today's standards**	**Visual inspection capability**	**Total**
Design ideas							
UV light	4	5	4	2	4	5	**4.04**
poison	1	1	2	5	1	5	2.20
sweeping	4	3	5	3	5	5	4.02
ultrasonic sound	4	4	5	2	1	5	3.60
High-pressure flow	5	3	5	3	4	5	**4.17**
blades	5	1	5	4	4	4	3.77
darkness	4	5	3	1	1	3	3.16
brushes	4	3	4	3	5	5	**3.89**
electric field	2	0	4	2	4	4	2.33
radio waves	0	0	3	1	1	0	0.67
gamma waves	4	4	3	1	1	4	3.07
heat	4	4	3	2	2	4	3.33
laser	3	0	4	5	4	5	3.16
acidic/basic conditions	2	0	0	0	0	0	0.53
electrolyzed sea water	5	3	3	4	1	4	3.56
suction cup	4	3	5	2	4	5	3.76
vibration	5	5	3	3	4	4	**4.20**
anchor-like scraping appendage	4	3	5	4	4	4	3.92

Each idea received a weighted score based on its fulfillment of the criteria with greater weight given to the more important criteria. Based on these results, it was concluded that UV light, high-pressure flow, vibration, and brushes were the best candidates for products. An electric field, radio waves, and acidic/basic conditions could not be conclusively evaluated as these designs have not been developed or assessed in past studies. Designs such as radio waves and acidic/basic conditions were eliminated due to their lack of compatibility with today's standards. Acidic/basic conditions would likely be detrimental to the environmental as the runoff would affect the pH of the water and the health of marine organisms. Radio waves would probably be ineffective in killing the fouling and might adversely affect the ship's signature leading to increased susceptibility.

Ultrasonic sound and a suction cup mechanism were considered as well. In order to kill the fouling, an extremely high frequency of sound would be required. Such a high

frequency sound would be difficult to isolate on the ship and would impact the surrounding marine environment. In a study conducted on the effect of low frequency sound on zebra mussels, it was concluded that acoustic control could be used for prevention of fouling but not for actual removal of the fouling. The sound does not actually kill fouling organisms, but the vibration of the ship prevents the settlement of fouling organisms as they deem it an incompatible substrate. In order to be effective, the vibrating mechanism would have to remain on at all times, which is not a likely option. A suction cup mechanism would significantly increase the grooming time because the vehicle would have to stop to suction the slime, proceed, and then pause again; the repetition of this procedure would significantly slow down the vehicle and result in increased grooming time.

UV Light Transmission Through Fiber Optic Cables

UV light was deemed a practical choice for an underwater cleaning tool. Wastewater treatment plants commonly use UV light to kill bacteria. An Israeli company recently developed a UV transmission system through a quartz tube using the same principles as fiber optic cables.[24] In a system developed by Atlantium, the quartz tube was used as a reactor and the water was bombarded with high amount of UV radiation. The quartz walls of the tube reflected the UV light so that it was transmitted through every drop of water. If ultraviolet light is concentrated on the hull, it should not be detrimental to the environment, since the UV rays will not be transmitted into the water. Thus, the recommendation is to transmit UV light through fiber optic cables, which will allow for maximal concentration of light on the hull surface.

The main drawback to the use of UV light is the time of application; however, increasing the intensity of the light can reduce the time of application. Degradation of the paint is also a concern as the paint may absorb UV radiation causing free radical reactions and the subsequent degradation of the polymers in the coating. Free radical reactions would pose a major environmental hazard as they could cause genetic abnormalities in marine organisms. However, these environmental hazards depend on the speed of the reaction and the conditions necessary for it to occur; the reaction might be a very slow process that likely would not have an immediate effect on the ship. In addition, an ideal design would be one in which the light would just be concentrated on the fouling organisms and one that would not penetrate through to the coating. Any negative impacts could be alleviated through the use of UV stabilizers.

[24] "Using UVs to kill water." Marcy 20076. http://www.primidi.com/2005/08/26.html

Recommendations for Brush Designs

Decision Factors

Brush designs must first be evaluated based on the type of coating they will be used against. Current AF coatings ablate over time and so it is critical to develop a grooming tool that limits the ablation of the coating. Second, the tool should not be easily clogged with fouling; otherwise, the cleaning of the grooming tool will result in increased expenditures and cleaning time. Third, the grooming mechanism should be simplistic enough such that it does not require a large expenditure of power. In the case of a fouling release coating, which the Navy does not currently use, the cleaning tool should avoid scratching of the paint. As soon as part of the coating is removed, a microniche for an organism's settlement is created thereby increasing the likelihood of heavier fouling. In the event that an epoxy coating is used, the aggressiveness of the cleaning tool is no longer a factor; however, the frequency of cleaning will have to increase to prevent any fouling growth. These brushes were designed to be aggressive enough to remove the fouling while maintaining the integrity of the coating, assuming than an AF coating, which is the norm on Navy ships, will be used. In the event that a more durable coating is used, the aggressiveness of the brushes may be increased as necessary.

Other evaluation criteria included ease of use and time of application. Future considerations will include bristle diameter, bristle density, and bristle spacing. The longer the bristle, the flimsier the brush is and the less force it applies to the hull surface.

Extended Bristle Brush

The extended bristle brush consists of a long stem with bristles attached. It is modeled on the brush seta of the amphibious freshwater crab *Geothelphusa dehaani*. We chose to model the brush based on the brush seta because it was effective in gill grooming. The main shortcoming, however, was that the brush did not entirely remove the fouling and a respiratory stream of water was needed. This raises questions about the brush's ability to clean the hull considering this design was not entirely effective for the crab. Nevertheless, the brush's simplicity and ease of use make it a viable option for hull-grooming. The grooming tool will consist of several of these brushes mounted in succession on the autonomous vehicle and will simultaneously groom the hull.

Assessment of Risk Factors

The bristle brush will simply brush the fouling into the water with minimal removal of the coating unless the brush pressure is significantly high. Because only a single type of brush is used, it may be necessary to increase the brush pressure. However, the bristles are non-abrasive and so the removal of large amounts of coating is not anticipated.

Technology for the extended bristle brush is currently available and so the practicality of this design is not a challenge. The brush is simplistic in nature and should not be difficult to manufacture. Due to the simplicity of the design, it will efficiently clean the hull surface in minimal time. Additional time will not be incurred in changing the bristle type while cleaning a particular area of the hull. Increased cleaning time will result if fouling

becomes embedded in the brush. The likelihood of fouling accumulating in the brush depends on the distance between each individual bristle; the goal of the design is to pack the maximum number of bristles onto the surface of the brush. The concern that arises with tight packing is increased abrasiveness although this can be varied by adjusting the pressure the brush applies against the hull. Further testing regarding the packing of the bristles, bristle diameter, and bristle width will need to be conducted to determine the appropriate level of brush aggressiveness.

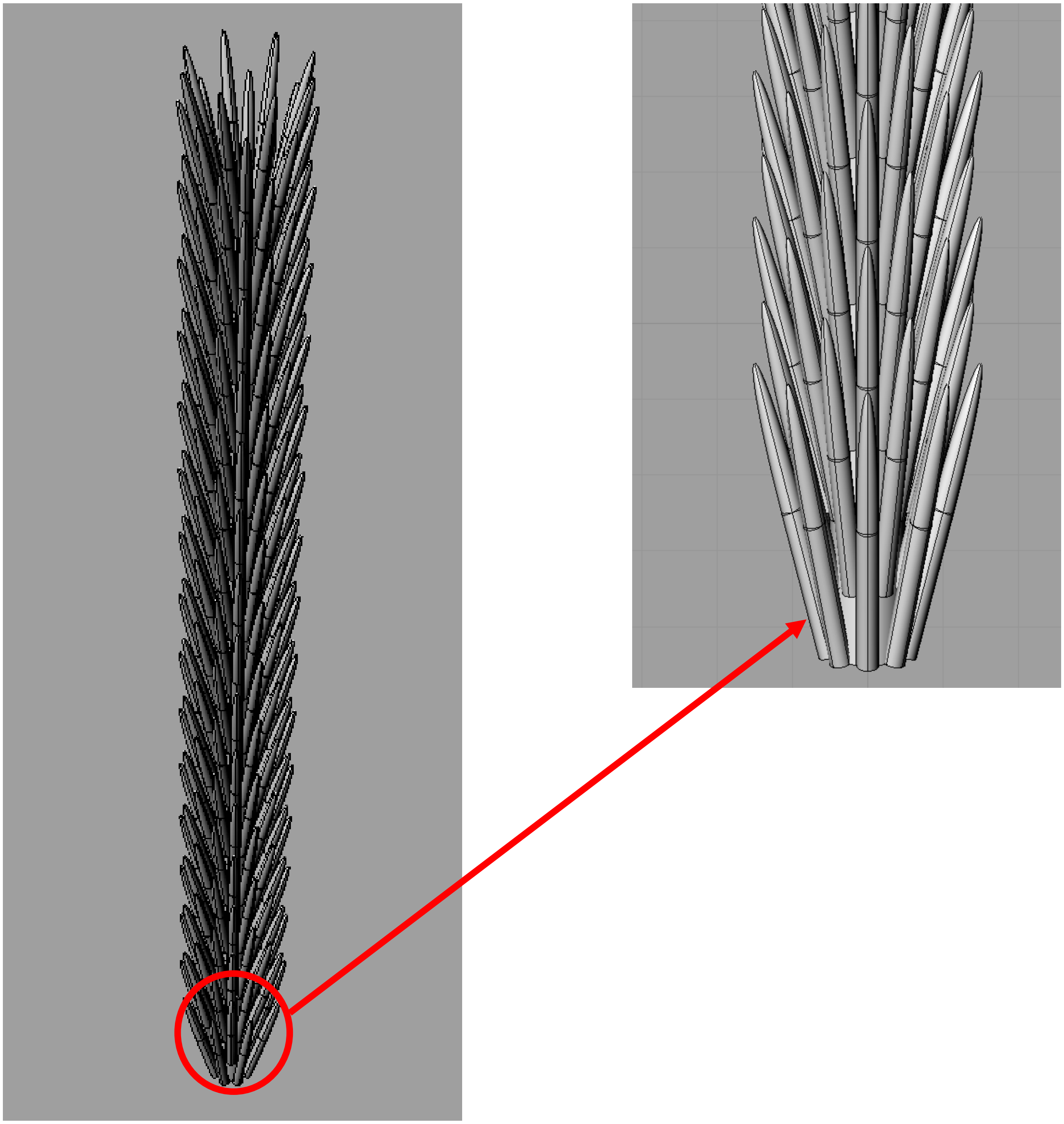

Figure 10: Extended bristle brush.

Scotch-Brite™ Paint Roller

This grooming tool involves rolling Scotch-Brite™ sponges around a paint roller and then rotating and vibrating the roller against the hull surface. The benefit of a roller is that it can target a greater surface area over a period of time and more efficiently than a simple sponge rubbing against the surface.

Assessment of Risk Factors

Scotch-Brite™ sponges likely provide the most abrasive form of cleaning action against the hull surface and therefore, may cause removal of the coating. However, the level of penetration may be adjusted so that the sponges only graze against the fouling and do not penetrate the coating. Scotch-Brite™ is commonly used in many household applications. Fashioning the material into a vibrating roller is a feasible technological application. A roller requires the least cleaning time and will not reduce vessel availability. The mechanism of action simply involves rotating a bar against a surface. If the brush is too abrasive, however, the effective life of the coating will be reduced. Additionally, no-scratch, heavy-duty sponges are available, which would provide maximal cleaning efficiently with little damage to the coating. Considering only one type of mechanism is used, this mechanism requires the shortest grooming time. Grooming time might be increased, however, if fouling becomes embedded in the sponges.

Rotary Brush

The rotary brush consists of rows of bristles mounted on a rotating cylinder that brushes against the hull surface. It is not an aggressive form of attack and so it will not cause significant peeling of the coating. Ablation of the coating will only occur if the brush speed and the force applied is large enough to penetrate the coating. If any unloading occurs, it will likely be minimal considering the brush's mode of action. A rotary brush includes sheaths of bristles that continuously brush against the hull surface.

Considering that the mode of action involves only one type of cleaning action, cleaning time will not be significantly increased. Increased cleaning time may result from the fact that each tool contains four sheaths of brushes that must complete one full rotation for every spot the vehicle lands on. More cycles may be required for areas that are heavily covered in slime resulting in additional cleaning time. However, the brushes are relatively compact, not bulky, and therefore complete a full rotation with relative ease. The rotary brush is modeled on already existing designs, specifically one available from the Sealeze company; thus, the brush is technologically viable.

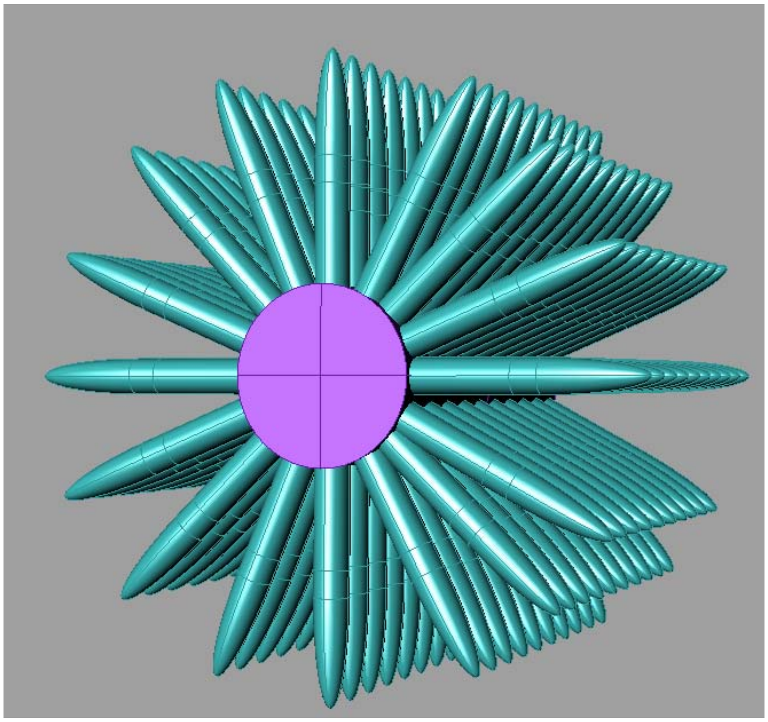

Figure 11: Rotary brush.

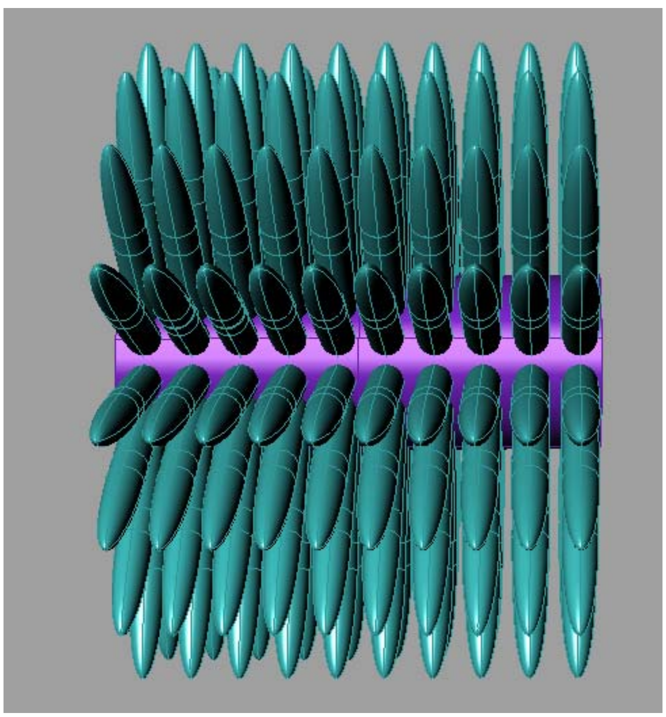

Figure 12: Face-on view of bristles in rotary brush.

Windshield Wiper cum Rotary Brush

This brush consists of a two-part mechanism with two different types of brushes. It will involve minimal ablation of the coating as the brushes are of varying strengths and aggressiveness. The windshield wiper brush constitutes one mechanism of action that involves reducing the adhesion strength of the slime and pushing it to one side; then, the rotating bristles physically remove the slime. The advantage of this design is that it reduces the aggressiveness of any one brush and allows the brushes to work in tandem to remove fouling while maintaining the integrity of the coating. Thus, it allows for protection of the coating.

While the technology for each part of the brush exists, the combination of the technologies poses some difficulty. Determining the feasibility of this brush will require further analysis of the design including dimensions, time required for each component to clean the hull, and the total surface area covered. The use of more than one type of brush will increase the amount of time required to clean the hull due to the fact that multiple brushes will become cumbersome. Further testing is required to determine how long each brush will be deployed and the time for transitioning between each type of brush.

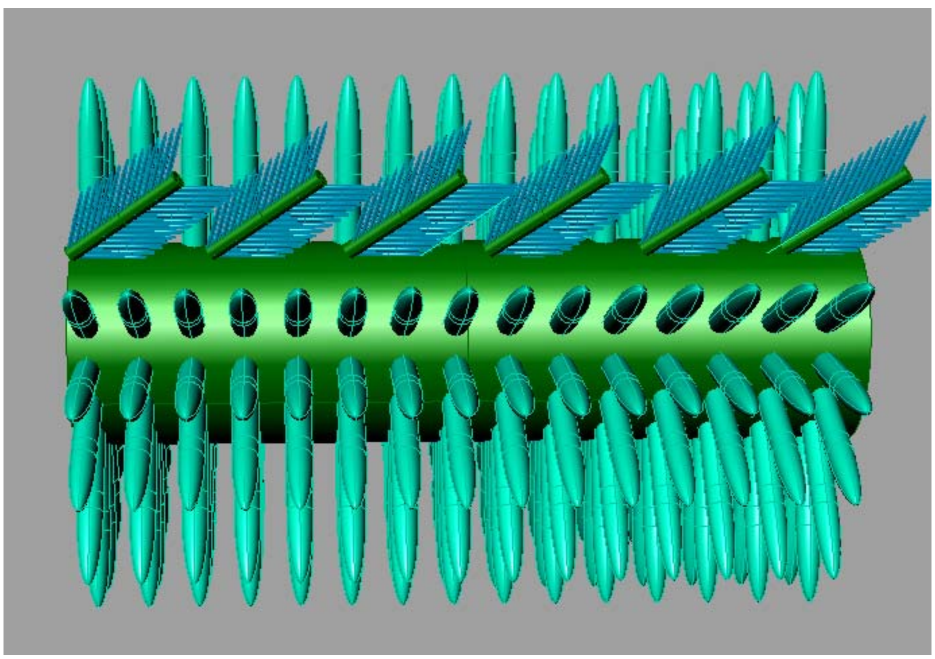

Figure 13: Windshield wiper/rotary brush with first row of bristles removed to display windshield wipers.

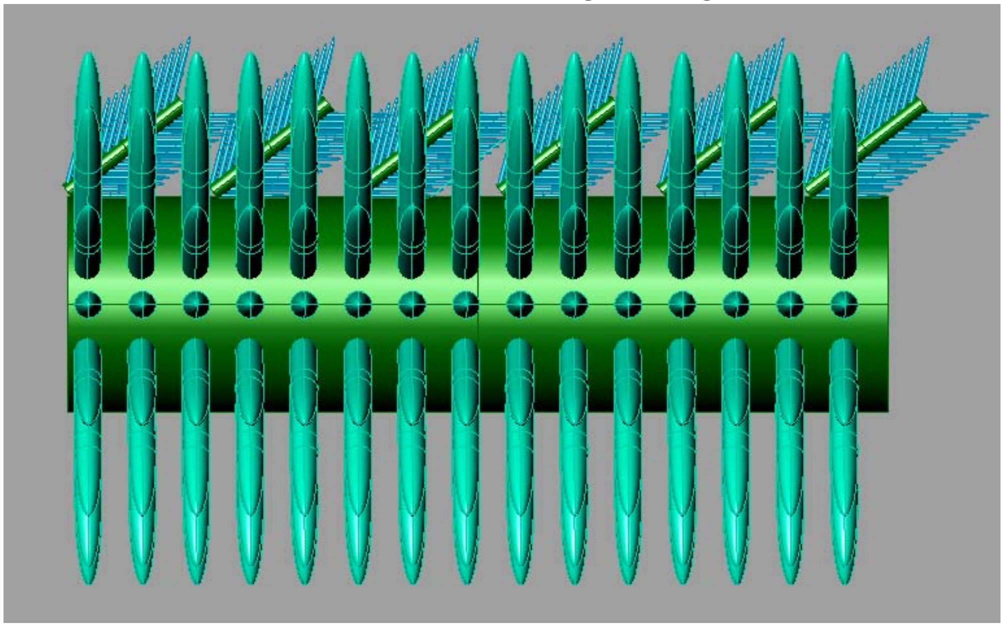

Figure 14: Face-on view of windshield wiper/rotary brush.

Multifunctional Brush

The multifunctional brush involves a dual mechanism of action. Long, extended bristles constitute one form and "hand-like" bristles constitute the second form. The long bristles are modeled on the setobranch setae used by crayfish and the hand-like structures are modeled on a mechanism used by shrimp. While the longer bristles brush against the surface, the hand-like structures will perform a sweeping action wiping away the microfouling from the hull surface.

Each type of brush is non-aggressive and the two types of brushes allow for a reduction in the aggressiveness of a single brush. Furthermore, the dual cleaning mechanism is efficient because it launches a twofold attack against fouling increasing the likelihood of slime removal. The dual cleaning action may be a hindrance in terms of total cleaning time as the use of two types of brushes will not be as efficient.

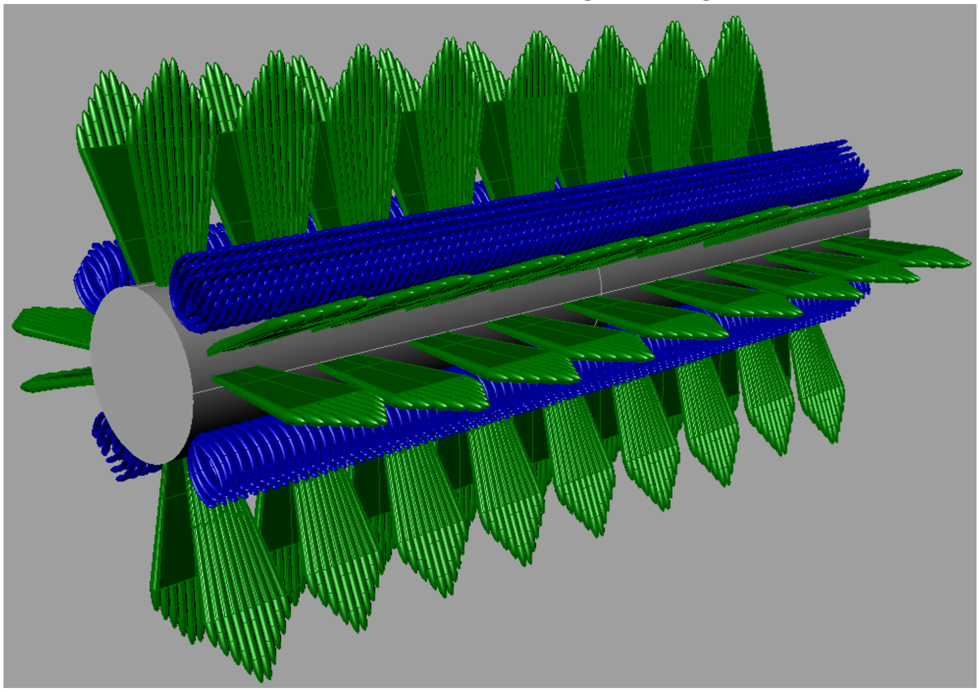

Figure 15: Multifunctional brush.

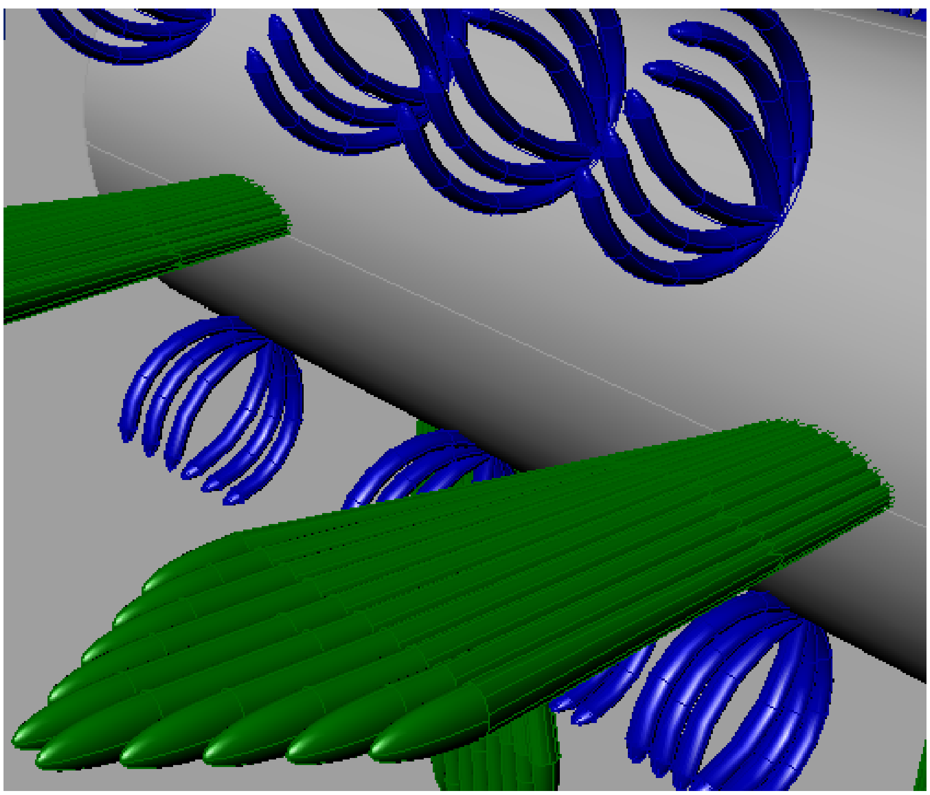

Figure 16: Close-up view with several bristles removed.

Bristle Material Analysis

Various bristle materials were researched for the brushes. Research indicated that the best material for the brushes is polypropylene due to its water-resistant properties. Polypropylene is a cross-linked polymer composed of nonpolar propyl groups that resists attraction to water. It remains stiff when exposed to water, has less than 0.2% water absorption, a long flex life, good springiness or flicking, and good bend recovery. Thus, it is expected to have a relatively long life in the marine environment. Other materials such as nylon retain more than ten times the amount of water, a significant drawback considering that the brush will be submerged for extended periods of time. The table below compares a variety of possible materials investigated for use in brush design.

Table 3 Comparison of brush materials. [25]

TABLE of PROPERTIES
The following definitions will help in understanding the properties in the table below.

Shape: Level refers to filament or wire that is straight. Crimped filament or wire is wavy and measured by amplitude and frequency and produces a denser appearing brush.
Flex Life: Amount of times a filament can be bent back and forth without damage.
Springiness or Flicking: How fast a filament snaps back to its original position after being bent.
Bend Recovery: A filament's ability to return to its original position after being bent for a short period of time.
Resistance to Set: A filament's ability to return to its original position after being bent for a long period of time.
Abrasion Resistance: A filament's ability to resist wear.
Water Absorption: The ability to retain water. Measured by percent of fiber weight.
Stiffness in Water: The ability of the filament to retain its original stiffness with full water absorption.

Properties	Nylon 6	Nylon 6.6	Nylon 6.12	Polypropylene	Polyester	Synthetic for Elevated Temp	Horsehair	Tampico (Plant)
Shape	Level or Crimp	Level or Crimp	Level or Crimp	Level or Crimp	Level or Crimp	Level	Level	Level
Flex Life	E	E	E	E	G	E	E	F
Springiness/Flicking	E	E	E	G	E	E	F	G
Bend Recovery	E	E	E	G	E	E	F	P
Resistance to set	G	G	G	F	G	G	G	F
Abrasion Resistance	E	E	E	F	G	E	F	P
Water Absorption	9%	9%	3%	<0.2%	<0.5%	9%	--	--
Stiffness in Water	F	F	G	E	E	G	F	P
Environment								
Working Temperature (degrees F)	200-230	200-230	200-230	180	200-230	250-300	na	na
Hot Water	G	G	G	E	E	G	P	E
Melting Point (degrees F)	410	500	415	320	430	495	--	--
Acidic	G	G	G	E	G	G	--	--
Alkaline	E	E	E	E	G	?	--	--
Petroleum Distillates	E	E	E	G	G	E	--	--
E = Excellent		**G = Good**			**F = Fair**		**P = Poor**	

[25] "High quality brush products for industrial applications." Sealeze. <http://www.sealeze.com/catalogs/brush_products_catalog.pdf>.

Recommendations for Future Research

Antifouling coatings such as the mPEG-DOPA polymer should be examined as a possible coating option for Navy ships. The polymer has yet to be synthesized on a mass scale; however, preliminary results based on microscale tests in the laboratory appear promising. It avoids the short lifespan of antifouling coatings that ablate easily and the fouling release coatings that require the ship to be in constant motion.

It is recommended that future research involve selection of one of the above brush designs and determination of the brush specifics. These specifics should include but not be limited to the number of bristles, bristle diameter, number of bristle per square centimeter, and length of bristle. Decreasing the length of the bristle will result in increase pressured and a more abrasive form of cleaning. The goal of the brush is to provide maximum cleaning efficiency with minimum aggressiveness. The brush will likely be a power brush and so energy and power considerations including rpm (revolutions per minute) will be considered. A contact with the Sealeze brush company has been established and they offer custom brush designs.

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